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# ***Trans*-stereospecific polymerization of butadiene and random copolymerization with styrene using borohydrido neodymium / magnesium dialkyl catalysts**

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## **Abstract**

The combination of a neodymium borohydride,  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$  (**1**) or  $\text{Cp}^*\text{Nd}(\text{BH}_4)_2(\text{THF})_x$  (**2**), with  $\text{Mg}^n\text{BuEt}$  (BEM), affords an efficient and highly selective (up to 96.7% 1,4-*trans*) catalyst for butadiene polymerization. In the presence of excesses of Mg co-catalyst, polymer chain transfer takes place between neodymium and magnesium, and significant amounts of 1,2-units are observed. When considered for butadiene-styrene statistical copolymerization, the catalytic system based on **2** showed a good ability to produce poly[(1,4-*trans*-butadiene)-*co*-styrene)], with strong impact of the Mg/Nd ratio on the yield and on the copolymer microstructure, including the percentage of inserted styrene (up to 16.9 mol %). Whatever the co-monomers concentration the polybutadiene backbone remained 1,4-*trans*. The precise microstructure of the polymers and copolymers was thoroughly analyzed by means of high resolution NMR spectroscopy (900 MHz) and MALDI-ToF spectrometry.

## Keywords

Stereospecific polymerization, *trans*-polybutadiene, styrene-butadiene copolymer, rare earths, microstructure, NMR.

## Introduction

The coordination polymerization of conjugated dienes is a topic of prime importance for numerous industrial applications requiring high performance rubber [1-3]. Whereas synthetic polyisoprene has seen a renewing interest in the polymer chemists' community during the last decade [4], polybutadiene (PB) still reached the highest industrial development. With the aim of obtaining mechanical behavior that can compete with Natural Rubber, research on polybutadienes has been oriented through obtaining highly *cis*-stereoregular polymers, using Ziegler-type catalysts in mild conditions based on transition metals [5-8], and rare earths [2,4,9,10]. The *trans*-polymerization of butadiene has been in turn less explored since the pioneer disclosures of Natta [11-13]. It mainly involves catalysts based on metals of the group IV [14,15], group V [16-18], chromium [19,20], iron [21,22], and also late transition metals like rhodium [23] or cobalt [24]. The resulting polymers display good hardness and abrasion resistance [25-28], which motivated the search for the development of new *trans*-selective catalytic systems. Among them, rare earths based catalysts can be efficient in the absence of aluminum co-catalysts, which is of great interest regarding the environmental impact. This is the case for allylic derivatives of the early lanthanides reported by the group of Taube in the middle 1990s. Up to 94% *1,4-trans*-selectivity in butadiene polymerization was achieved using allyl neodymium complexes as single component catalysts [29], and up to 96 % (from Infra Red determination) in the presence of chlorinated additives [30]. More recently, Okuda reported the borate activation of a mixed La/Al half-metallocene to yield 90-91.9 % *trans*-polybutadiene [31]. Using rare earths pre-catalysts supported by bulky hetero-element ligands, associated to a combination of an aluminum co-catalyst and a boron activator, Cui *et al.* obtained *trans*-stereoregular (*ca.* 91%) polybutadienes [32,33]. It is noteworthy that compared to transition metals based catalysts, the afore-mentioned catalysts based on rare earths led to *trans*-PB with narrower dispersity, and thus a higher degree of control of the catalysis.

We disclosed in these recent years a very efficient catalytic system for the polymerization of isoprene, based on the combination of the borohydride  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$  as pre-catalyst with a

magnesium dialkyl, which afforded a polymer with a high degree of *trans*-stereoregularity [34,35], along with a good control of macromolecular data. To our knowledge, regarding the *trans*-selective polymerization of butadiene, Mg dialkyl has been scarcely reported as co-catalyst associated with neodymium versatate [36], alkoxide/aryloxide [37], constrained geometry half-sandwich [38], and more recently with a phosphazene derivative of this lanthanide element [39]. Due to the importance of rare earths compounds in butadiene polymerization catalysis and related applications, and considering the little number of *trans*-selective catalysts by comparison with the *cis*-selective ones, we aimed to explore the potential of the above mentioned borohydrido Nd/Mg combination towards the polymerization of butadiene. Such study was also of particular interest since the selectivity is not necessarily transposable from isoprene to butadiene [19,21,39].

The insertion of styrene into polydienes is a good way to reinforce industrial materials [8]. Coordinative butadiene-styrene random copolymerization using lanthanide-based catalysts was developed in this frame in the last two decades and it afforded mostly copolymers with styrene inserted into a *cis*-regular polydiene backbone [40-44]. Similar copolymers having *trans*-polydiene arrangement were much less reported [14,37]. Using a neodymium-based organometallic pre-catalyst associated with an equivalent amount of dialkylmagnesium reagent, up to 32% molar styrene was randomly inserted into polyisoprene without modifying the *trans*-stereoregularity of the polyisoprene backbone [45]. In chain transfer copolymerization conditions, *ie* in excess of Mg co-catalyst, the styrene was inserted at a 49 % molar ratio [46].

In this paper we describe the application of the dual borohydrido Nd/Mg catalytic system to the homo-polymerization of butadiene, and its co-polymerization with styrene. The influence of different parameters was considered: the amount of the magnesium dialkyl and the reaction temperature for homopolymerization; the monomers feed and the amount of magnesium dialkyl for copolymerization. To our knowledge, the *trans*-selectivity obtained is one of the highest observed for a rare earth catalyst, along with fair control over the macromolecular data with equimolar amounts of Mg dialkyl. Rare examples of poly(1,4-*trans*-butadiene-co-styrene) were received in copolymerization conditions, containing up to ca 17 molar % of inserted styrene.

## Experimental

**Materials.** All operations were carried out in a glove box or using Schlenk techniques. Toluene (Chem-Lab; 99.5%) was purified through alumina column (Mbraun SPS), degassed

by argon bubbling, dried on molecular sieves (4 Å) and stored in the glove box at room temperature. Butadiene (Linde; 99.5%) was purified by neutralizing protic impurities with a solution of  $\text{Mg}^n\text{BuEt}$  (abbreviated as BEM) in toluene and then distilled from the mixture and stored in a gas cylinder at room temperature. Styrene (Acros; stabilized with 4-tert-butylcatechol, 99%) was dried with  $\text{CaH}_2$  for three days, then degassed using the freeze-pump-thaw method, distilled under vacuum, and finally stored over molecular sieves (3 Å), in the glove box, at  $-24\text{ }^\circ\text{C}$ . BEM (Texas Alkyls; 20 wt % in heptane),  $\text{Mg}^n(\text{Bu})_2$  (Aldrich; 1.0 M in heptane), pentamethylcyclopentadiene  $\text{Cp}^*\text{H}$  (Aldrich; 95%), 9-benzhydrylidene-10-anthrone (Acros; 95%), were used as received and stored in the glove box at room temperature. Technical methanol (P. Brabant), HCl solution (34 wt % in water) and 2,6-Di-tert-butyl-4-methylphenol (BHT) (Aldrich) were used as received and stored at room temperature.

The pre-catalyst  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$  (**1**) was synthesized from  $\text{NdCl}_3(\text{THF})_3$  as reported in the literature [47,48] and it was stored in a glove box at room temperature. The half-sandwich  $\text{Cp}^*\text{Nd}(\text{BH}_4)_2(\text{THF})_x$  (**2**) was synthesized *in situ* by using the B/A route [49], *ie* adding  $\text{Cp}^*\text{H}$  on the **1**/BEM catalytic system, and not isolated. Alternatively, ionic metathesis from **1** and following the procedure described in previous works [47], afforded a complex (**2'**) that was isolated and stored in the glove box at room temperature. This compound has two THF molecules per Nd atom when freshly isolated [35], but we observed that it displayed a propensity to desolvate and clusterize [50], affecting the THF amounts and solubility properties. As an example,  $^1\text{H}$  NMR integration in  $\text{C}_5\text{D}_5\text{N}$  gave  $\text{Cp}^*\text{Nd}(\text{BH}_4)_{1.9}(\text{THF})_{0.6}$ <sup>1</sup> for the batch **2'**.

**Butadiene polymerization.** In a typical example (run 1), in a glove box, a desired amount of pre-catalyst **1** (40.5 mg, 100  $\mu\text{mol}$ ) was introduced into a preparation tube with 5 mL of toluene, and shaken until dissolution. Then were added to the blue solution  $\text{Cp}^*\text{H}$  (13.6 mg, 100  $\mu\text{mol}$ ), BEM (55.2 mg, 100  $\mu\text{mol}$ ) and a few amount of a 20% butadiene solution in toluene (2 drops). One fifth (20  $\mu\text{mol}$ ) of the resulting green solution was weighed in a polymerization tube equipped with a magnetic bar. The complement of BEM was then added (10  $\mu\text{mol}$ ) to reach the desired Mg/Nd ratio. After addition of the 20% butadiene solution in toluene (5.41 g, 20 mmol) and filling up to 11.5 mL with toluene, the polymerization tube was sealed and removed from the glove box. Alternatively (run 9), the pre-catalyst **2'** (8.6 mg, 20

<sup>1</sup> The deviation from a  $\text{Cp}^*\text{Nd}(\text{BH}_4)_2(\text{THF})_{0.6}$  formula was attributed to the difficulty of properly integrate the signals due to paramagnetism of the lanthanide metal.

$\mu\text{mol}$ ) was introduced into a 100 mL glass Schlenk tube equipped with a magnetic bar. Then BEM (15  $\mu\text{L}$ , 20  $\mu\text{mol}$ ) and toluene (10 mL) were added to the Schlenk tube *via* a micro-syringe and a syringe, respectively. After closure, the Schlenk tube was removed from the glove box and frozen by liquid nitrogen. Butadiene (1.1 g, 20 mmol) was condensed into the frozen solution, through a septum. Whatever the preparation method, the solution was heated to the reaction temperature and maintained under constant magnetic stirring for the desired reaction time. Meantime, a solution of 20 mg of BHT as stabilizing agent dissolved into 10 mL of toluene was degassed by argon bubbling. At the end of the reaction time, the degassed BHT solution was added to the resulting solution, under constant magnetic stirring and argon flush, to quench the polymerization. The white powder was precipitated into 100 mL of cold methanol, filtered and dried under vacuum for 12 h (yield = 96 %, run 1).

Polymerization batch dedicated to  $^{13}\text{C}$  NMR end-group determination: 80  $\mu\text{mol}$  of **2'** were used with 200  $\mu\text{mol}$  of BEM, other conditions being identical to previously described. The yield of this run was 41%. The SEC analysis (uncorrected, PS standards) of the resulting polymer gave a number average molecular weight of 7,000 g/mol (PDI = 1.40) and the  $^{13}\text{C}$  NMR analysis was sufficiently accurate to identify all signals, including those corresponding to end-groups, and to the usual regio-irregularities.

**Butadiene-styrene copolymerization.** The butadiene-styrene copolymerization was performed in the same reactor as for butadiene homopolymerization. The same procedure as previously described was used, but in addition, styrene (2.1 g, 20 mmol, run 16 given as an example) was incorporated into the Schlenk tube just after the toluene. The toluene quantity was adjusted to fulfill the total volume of 11.5 mL, whatever the butadiene and styrene amounts.

Copolymerization batch dedicated to MALDI-ToF analysis: pre-catalyst **1** (40.5 mg, 100  $\mu\text{mol}$ ),  $\text{Cp}^*\text{H}$  (13.6 mg, 100  $\mu\text{mol}$ ),  $\text{Mg}(\text{nBu})_2$  (150  $\mu\text{L}$ , 150  $\mu\text{mol}$ ), butadiene (1.1 g, 20 mmol), styrene (2.1 g, 20 mmol) and toluene (filled up to 11,5 mL of total volume). The dialkylmagnesium compound was chosen in order to initiate polymerization with only one type of alkyl group (butyl). The sealed polymerization Schlenk was heated up to 50 °C and magnetically stirred for 15 minutes. A solution of 9-benzhydrylidene-10-anthrone (90 mg, 250  $\mu\text{mol}$ ) dissolved into dry toluene (2.5 mL) was added to the resulting solution, under constant magnetic stirring and argon flush. This compound was used to tag the living chains with a functional group in order to allow a better detection by MALDI-ToF technique. At the time of addition, the light green solution turned to black and rapidly to dark green.

Precipitation into 100 mL of cold methanol afforded a pale yellow powder, which was filtered, washed again with methanol, and dried under vacuum for 12 h.

**Polymer characterization.** Homo and copolymers were characterized by liquid  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectroscopy for microstructure determination, and by size exclusion chromatography (SEC) for the number-average molecular weight and the dispersity determination. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance 300 instrument at 300 K, in  $\text{CDCl}_3$  and  $\text{C}_2\text{D}_2\text{Cl}_4$  for polybutadiene and poly(butadiene-*co*-styrene), respectively. Calibration peaks for these solvents are 7.26 ppm ( $^1\text{H}$ ) and 77.36 ppm [ $^{13}\text{C}$ ] for  $\text{CDCl}_3$ , and 5.91 ppm ( $^1\text{H}$ ) and 74.2 ppm ( $^{13}\text{C}$ ) [52] for  $\text{C}_2\text{D}_2\text{Cl}_4$ . One polybutadiene sample was also analyzed on a Bruker Avance III 900 instrument at 900 MHz (300 K,  $\text{CDCl}_3$ ). SEC analyses were performed in THF at 40 °C (1 mL.min $^{-1}$ ) with a Waters apparatus, calibrated with polystyrene standards, and composed of a Waters SIS HPLC pump, a Waters 410 refractometer, and Waters Styragel columns (HR2, HR3, HR5 and HR5E). MALDI-ToF measurements were performed with an Ultraflex II apparatus with positive reflectron MS mode, dithranol matrix, trifluoroacetic acid as cationizing agent and steel target. The obtained spectrum was compared with simulated spectra based on model compounds having a butyl initiator, n butadiene motives, m styrene motives, a termination derived from the tag used to quench the polymerization and an H atom resulting from the cationization process. Each peak abscissa fitted within 0.1 g/mol of precision between the spectrum and the simulation. The isotopic distributions, based on  $^{13}\text{C}$  natural abundance, fitted within a few percent of relative amounts (see Supplementary Data).

## Results and discussion

**Butadiene homopolymerization.** Polymerization experiments were first carried out with  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$  (**1**) as pre-catalyst. Representative results are gathered in table 1.

The  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$  / BEM catalyst shows a good efficiency *vs.* butadiene polymerization with complete conversion in 2 h at 50 °C with 1 equiv BEM per Nd (run 1). The average activity of 27,000 g polymer/mol Nd/h is in between the values reported by Liu *et al.* (ca 18,000 g polymer/mol catalyst/h) [32] and by Taube (33,000 g polymer/mol Nd/h) [29]. Using a chromium-based pre-catalyst and MMAO, Nakayama *et al.* synthesized quite perfect 1,4-*trans*-polybutadiene (> 99%), but with much lower activity (0.3 kg polymer/mol catalyst/h) [21]. The SEC analysis reveals a monomodal character of the elution peak along with narrow dispersity, which speaks in favour of the uniqueness of active species. One can

expect a theoretical  $M_n$  value of 27,000 g/mol considering two chains growing per Nd atom (1 chain growing per alkyl initiating group). This data is in fair accordance with the experimental  $M_n$  value determined by SEC (49,000, run 1) after application of a correction factor of 0.5 [53-55]. Interestingly, the catalyst is highly 1,4-*trans*-selective (> 95 %). This result could be expected by view of previous results in the literature with Ln/Mg catalytic combinations applied to isoprene polymerization, even if the level of selectivity in conjugated dienes polymerization is not necessarily transferable from butadiene to isoprene monomer as previously noticed [19,21,39].

**Table 1.** Polymerization of butadiene with  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$  (**1**) / BEM

Run <sup>a</sup>	[Mg]/[Nd]	Time (h)	Isolated Yield (%)	Selectivity <sup>b</sup> (%)			$M_n$ <sup>c</sup> (g.mol <sup>-1</sup> ) ( $\bar{D}$ <sup>d</sup> )	$(M_n)_{th}$ <sup>e</sup> (g.mol <sup>-1</sup> )
				1,4- <i>trans</i>	1,4- <i>cis</i>	1,2		
1	1	2	96	95.0	3.5	1.5	49000 (1.29)	49000
2	2	2	54	95.5	2.4	2.1	19000 (1.28)	27600
3	3	2	16	93.0	2.4	4.6	5500 (1.20)	8200
4	5	2	8	88.0	3.1	8.9	3900 (1.24)	4100
5	5	8	20	89.9	2.1	8.0	3900 (1.43)	10200
6	5	20	37	90.4	1.3	8.3	5500 (3.00)	18900
7	10	20	18	80.7	3.5	15.8	3800 (2.90)	9200

a: Reactions at 50 °C, in 10 mL of toluene; pre-catalyst:  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$  20  $\mu\text{mol}$ ; co-catalyst: BEM; [butadiene]/[Nd] = 1000.

b: Determined by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy in CDCl<sub>3</sub>.

c: Number-average molecular weight measured by SEC with reference to PS standards. No correction factor applied.

d: Dispersity index measured by SEC:  $\bar{D} = M_w/M_n$ .

e: Theoretical Number-average molecular weight based on the yield and calculated by reference to the value of run 1, in the absence of Nd/Mg transfer:  $(M_n)_{th} = (M_n)_{run1} \times \text{Yield} / (\text{Yield})_{run1}$ .

With additional amounts of BEM, the activity severely decreased (runs 2-4, table 1). The polymer yield falls from 96 % (Mg/Nd = 1, run 1) down to 8 % (Mg/Nd = 5, run 4) within a 2- hour period. Meanwhile, the 1,4-*trans* selectivity was found to decrease, along with the regular increase of 1,2 defects (up to *ca.* 8% for 5 equiv Mg, run 4). Regarding the



macromolecular data, one could observe that the measured  $M_n$  values are lower than expected on the strict basis of the decrease of conversion. For instance, from run 1 to run 2, and considering only the yield as specified in Table 1, the  $M_n$  should be divided by a 0.96/0.54 factor, reaching the value of 27600 (column  $(M_n)_{th}$ )<sup>2</sup>. In fact, the measured  $M_n$  is 19000 for run 2, which is significantly lower than expected. The hypothesis of some chain transfer during the polymerization process between neodymium and magnesium metals [56] can thus be advanced to account for the lowering of the molecular weights. The same reasoning can be made runs 3 and 4 in Table 1, the more the BEM quantity, the shorter the polymer chains. Moreover, dispersities remain in a narrow range, which confirms this interpretation. With longer reaction times (runs 5 and 6) and higher BEM amount (10 equiv, run 7), the process is less controlled as shown by the macromolecular data. It is however worth to be noted that the selectivity remains fairly 1,4-*trans* in that case (15.8 % of 1,2- defects, run 7). Similar tendency in terms of evolution of the selectivity with the increase of BEM amounts had been observed with isoprene [57,58]. But the activity of the catalyst did not decrease in such an extent, and the transfer efficiency was close to 100 %, which marks here clear differences in behavior between isoprene and butadiene.

With a pre-catalyst having one  $Cp^*$  ( $Cp^* = C_5Me_5$ ) ligand in the coordination sphere of the metal, the system was slightly less active than with pre-catalyst **1** (runs 8, 10, 11, table 2, vs runs 1-3, table 1). This was a bit surprising with regards to previously mentioned isoprene polymerization studies [49,59,60].

**Table 2.** Polymerization of butadiene with  $Cp^*Nd(BH_4)_2(THF)_x$  (**2**) / BEM

Run <sup>a</sup>	[Mg]/[Nd]	T (°C)	Isolated Yield (%)	Selectivity <sup>b</sup> (%)			$M_n$ <sup>c</sup> (g.mol <sup>-1</sup> )	$\bar{D}$ <sup>d</sup>
				1,4- <i>trans</i>	1,4- <i>cis</i>	1,2		
8	1	50	43	96.7	1.9	1.4	47000	1.38
9 <sup>e</sup>	1	50	70	95.3	3.1	1.6	100000	1.28
10 <sup>f</sup>	1	50	43	95.0	1.9	1.4	55000	2.20
11	2	50	43	95.3	2.2	2.5	42000	1.77
12	3	50	16	91.5	1.7	6.8	6700	1.35
13 <sup>g</sup>	5	50	24	88.7	1.2	10.1	6600	2.60
14 <sup>g</sup>	10	50	18	83.1	1.1	15.8	2500	2.00
15 <sup>e</sup>	1	30	14	96.4	2.0	1.6	34000	1.20

<sup>2</sup> We chose to refer to the  $M_n$  value of run 1 to overcome the PS calibration of the SEC.

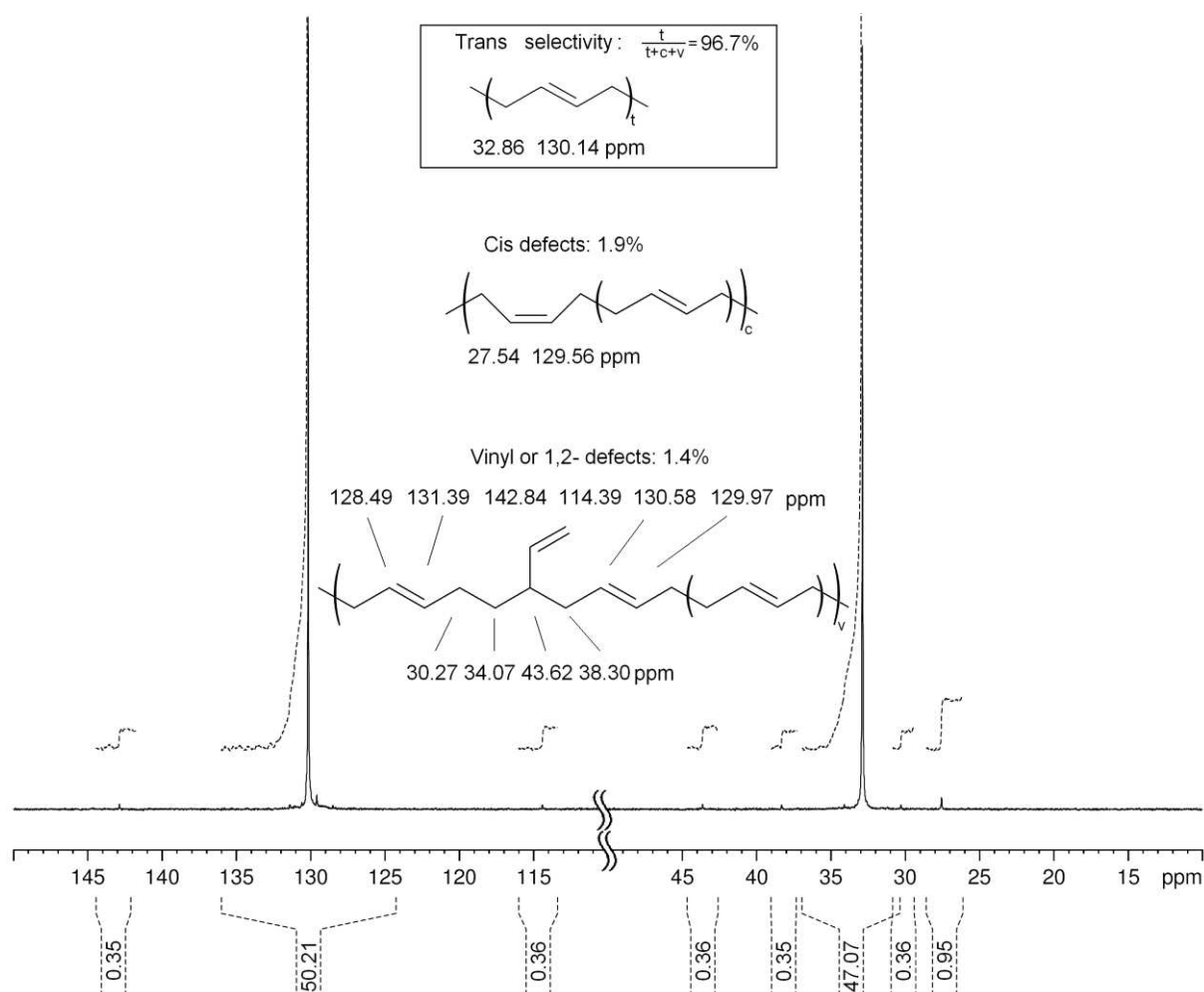
- a: 2 h reaction in 10 mL of toluene; pre-catalyst:  $\text{Cp}^*\text{Nd}(\text{BH}_4)_2(\text{THF})_x$  synthesized *in situ* from  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$  (20  $\mu\text{mol}$ ), 1 equiv  $\text{HCp}^*$  and 0,5 equiv  $\text{BEM}^3$ ; co-catalyst:  $\text{BEM}$ ;  $[\text{butadiene}]/[\text{Nd}] = 1000$
- b: Determined by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy,  $\text{CDCl}_3$
- c: Number-average molecular weight measured by SEC
- d: Dispersity index measured by SEC:  $\text{Đ} = M_w/M_n$
- e: Fresh batch of isolated  $\text{Cp}^*\text{Nd}(\text{BH}_4)_2(\text{THF})_x$
- f: Older batch of isolated  $\text{Cp}^*\text{Nd}(\text{BH}_4)_2(\text{THF})_x$
- g: Duration 20 h

A main difference between the two pre-catalysts is the higher *trans*-character of the polymerization when using the half-sandwich (up to 96.7 % 1,4-*trans*, run 8) vs. **1** as pre-catalyst. This observation corroborates well our previous reports related to isoprene polymerization. For  $\text{BEM}$  amounts higher than 2 equiv (runs 12-14), and as already encountered with **1**, the activity dramatically decreased: only 24 % yield of isolated polymer was obtained in 20 h in the presence of 10  $\text{BEM}$  equiv (run 14). The *trans*-selectivity was also strongly affected, as it could be anticipated from the results with pre-catalyst **1**. Running the polymerization at 30 °C (run 15) instead of 50 °C strongly impacted the polymer yield, which was limited to 14% in the former case (same batch of catalyst, run 9). These results are similar to those obtained by Terrier *et al.* [58] on isoprene polymerization with the catalytic system **1** /  $\text{BEM}$ . SEC analyses revealed quite narrow SEC traces for little amounts of  $\text{Mg}$  co-catalyst, but broadening when the  $\text{BEM}$  quantity was increased (runs 13, 14).  $M_n$  values decreased in general with higher quantities of  $\text{BEM}$ , which speaks in favour of a certain percentage of transfer reactions, but not in a controlled manner, with a behavior similar to that observed using **1**. This observation is in line with previous butadiene/ethylene  $\text{Nd}/\text{Mg}$  mediated copolymerization studies, in which the chain transfer between the two metals is described to be slow compared to chain propagation [61].

The structural determination of the received polybutadienes was carried out by means of  $^1\text{H}$  and  $^{13}\text{C}$  NMR analysis, and by careful comparison with data available from the literature.  $^1\text{H}$  NMR spectrum was first recorded at 300 MHz (a typical example is given in Figure S1, see Supplementary data). From the chemical shift and the shape of the signal at 5.41 ppm, it was possible to assume that the polymer was highly 1,4-regular, but a precise quantification of the *cis*-/*trans*- ratio required  $^{13}\text{C}$  NMR analysis. The  $^{13}\text{C}$  NMR spectrum of polybutadiene of run

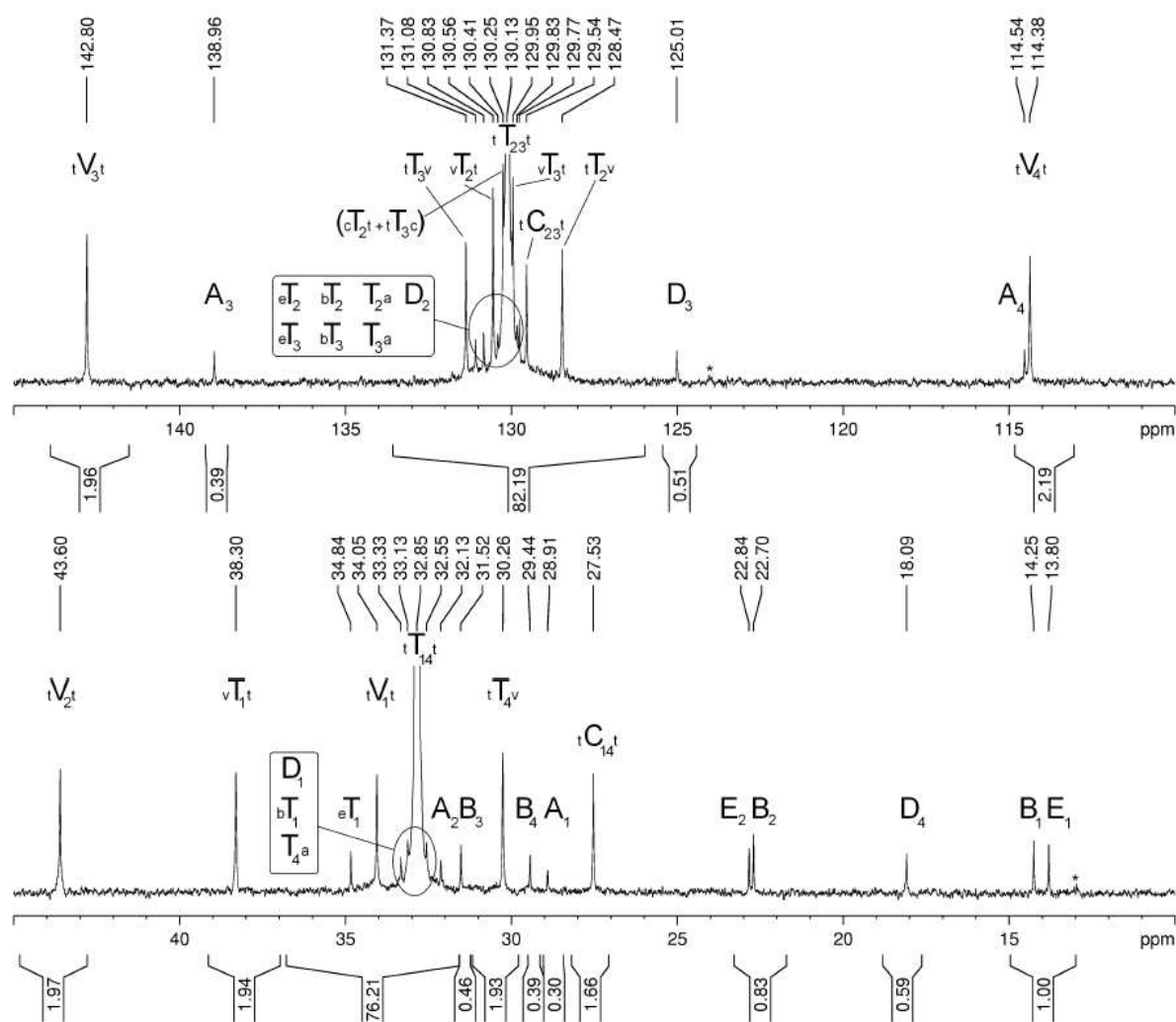
<sup>3</sup> The polymerization reactions were initially performed with isolated half-sandwich  $\text{Cp}^*\text{Nd}(\text{BH}_4)_2(\text{THF})_x$  with  $x = 0.6$  (from  $^1\text{H}$  NMR) but the results were found to strongly depend on the aging of the batch of complex. Actually, this compound is known to desolvate with time, leading progressively to clustering into poorly soluble  $[\text{Cp}^*\text{Nd}(\text{BH}_4)_2]_6$  [50]. In order to overcome the question of the desolvation of the pre-catalyst, we carried out experiments by using a catalyst prepared *in situ* by the B/A route methodology [49].

8 is shown on figure 1. The selectivity was calculated from relative integration of the methylene signals at 32.85 (stereo-regular *1,4-trans* polybutadiene), 27.53 (*1,4-cis* defects), and 34.05 or 38.30 ppm (vinyl defects) [62-64].



**Figure 1.**  $^{13}\text{C}$  NMR spectrum of polymer from run 8 ( $\text{CDCl}_3$ ).

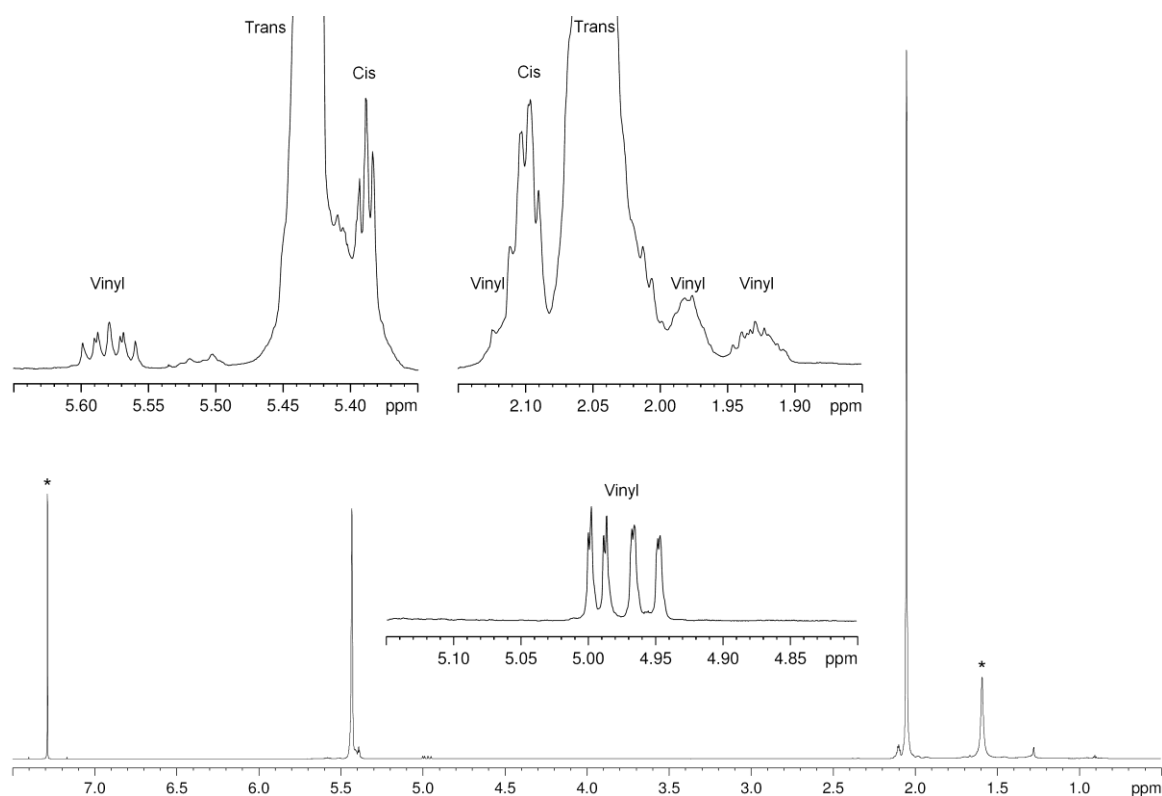
Careful analysis of the spectrum of a low  $M_n$  ( $2000 \text{ gmol}^{-1}$ ) sample, specially synthesized with Mg/Nd ratio of 2.5 (see details in experimental section) for end-groups analysis, allowed assignment of all signals (see figure 2, a and b), *i.e* corresponding to the microstructure with regio errors (T *trans*, C *cis*, V vinyl), but also end-groups coming from initiation by Et or Bu (E and B, respectively), and those resulting from the quenching of the growing chain (D and A) by hydrolysis. The naming convention is given after Makhyanov [64] and is detailed in the Supplementary Data.



**Figure 2.**  $^{13}\text{C}$  NMR spectrum of a low  $M_n$  *trans*-polybutadiene with full assignment of signals:  $\text{Csp}^3$  (bottom) and  $\text{Csp}^2$  (top) regions ( $\text{CDCl}_3$ , naming convention for tags, see Supplementary Data). \* suspected traces of a *cis* configuration for some ethylidene  $[=\text{CH}-\text{CH}_3]$  terminal groups.

An alternative approach for measuring the *trans*-/*cis*-vinyl composition was tentatively made by  $^1\text{H}$  NMR at very high field (900 MHz). The resulting spectrum, reported on Figure 3, showed clear resonances for each type of motive affording more evidences about the polymer microstructure. To the best of our knowledge, this spectrum displays the best defined  $^1\text{H}$  shapes recorded up to date for a *trans*-polybutadiene [64]. However, the resolution remained insufficient to allow a more reliable quantification compared to the  $^{13}\text{C}$  NMR.<sup>4</sup>

<sup>4</sup> In particular, the 1,4-*cis* amount was found difficult to identify accurately in the  $^1\text{H}$  NMR spectrum, since the *cis* signal was superimposed with residual vinyl ones. Hence, the microstructure of all the polymers in this work was reported using the  $^{13}\text{C}$  NMR method.



**Figure 3:** High resolution  $^1\text{H}$  NMR spectrum (900 MHz) of polybutadiene sample as synthesized in run 1 ( $\text{CDCl}_3$ ); \* solvent impurities and residual H resonance.

**Butadiene-styrene statistical copolymerization.** The influence of the co-monomers concentrations in the feed and the magnesium to neodymium ratio were examined, with respect to the reaction yield, the copolymer microstructure and the macromolecular data. The temperature and the reaction time were set to 50 °C and two hours, respectively, unless specifically indicated. Selected results are gathered in table 3.

In a general manner, it was found that the presence of styrene monomer slows down the polymerization rate: with equimolar amounts of styrene and butadiene, the isolated polymer yield was 22 % after 2 hours of reaction (run 16), whereas up to 70 % yield was observed in homopolymerization of butadiene (run 9). Increasing the quantity of styrene in the feed affords a much lower yield of only 10 % (run 17). It is noteworthy that with a feed rich in butadiene, the presence of 20 % styrene yet impacted negatively the rate of the polymerization (29 % yield, run 18).

**Table 3.** Butadiene-styrene statistical copolymerization with Cp\*Nd(BH<sub>4</sub>)<sub>2</sub>(THF)<sub>x</sub> (**2**) / BEM (B = butadiene, S = Styrene).

Run <sup>a</sup>	[Mg]/[Nd]	Yield (%) <sup>b</sup>	B/S in the feed (mmol)	B/S in the copolymer (mol%) <sup>b</sup>	Selectivity <sup>c</sup> (% in PB)			M <sub>n</sub> g mol <sup>-1</sup> ( $\bar{D}$ <sup>d</sup> )
					<i>1,4-trans</i>	<i>1,4-cis</i>	<i>1,2</i>	
9	1	70	20/0	100/0	95.3	3.1	1.6	100000 (1.28)
16	1	22	20/20	96.2/3.8	96.4	2.2	1.4	58000 (1.27)
17	1	10	20/80	83.1/16.9	97.2	2.2	0.6	97000 (1.56)
18	1	29	80/20	98.6/1.4	95.8	2.8	1.4	240000 (1.44)
19	3	4	20/20	94.7/5.3	93.2	1.7	5.1	4400 (1.53)
20 <sup>e</sup>	10	16	20/20	86.7/13.3	87.3	2.0	10.7	6800 (2.49)

a: 2 h reaction at 50 °C; solvent: toluene filled up to 11.5 mL of total volume; pre-catalyst: Cp\*Nd(BH<sub>4</sub>)<sub>1.9</sub>(THF)<sub>0.6</sub> 20 μmol; co-catalyst: BEM

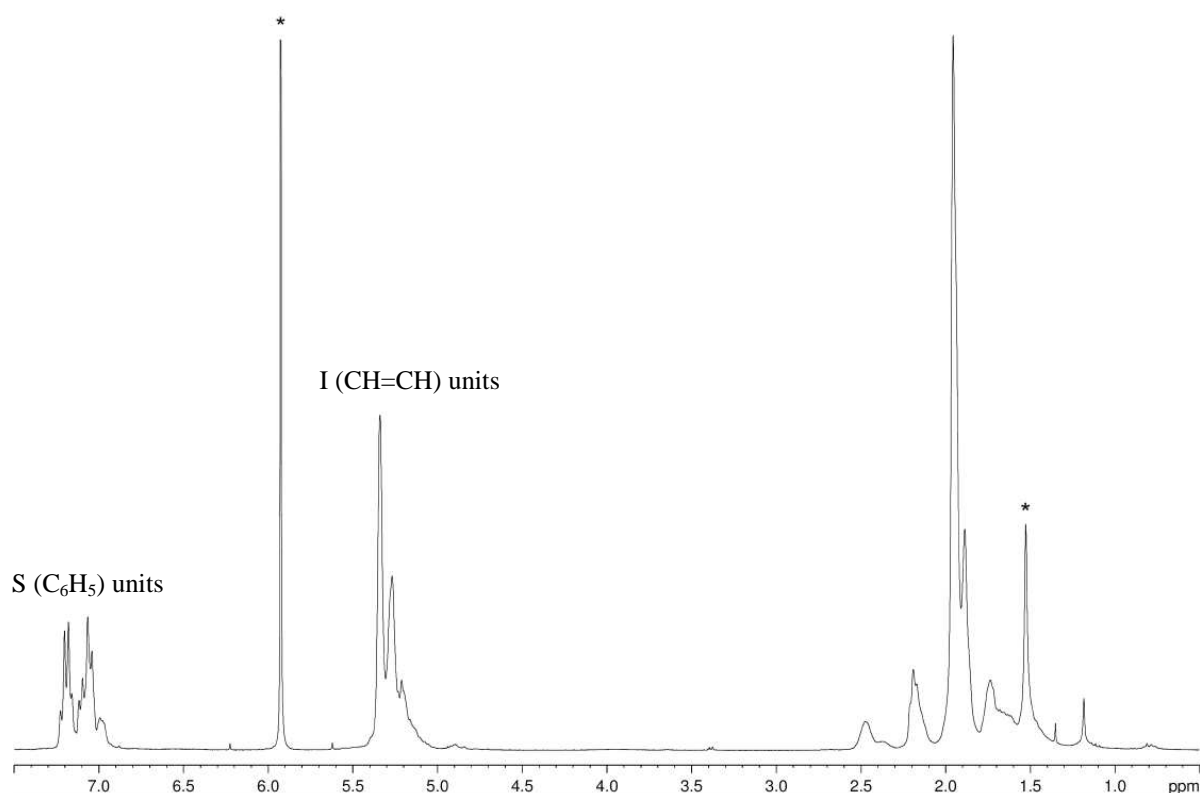
b: Based on total monomer consumption

c: Determined by <sup>1</sup>H and <sup>13</sup>C NMR in CDCl<sub>3</sub>

d: Number-average molecular weight measured by SEC; Dispersity index measured by SEC:  $\bar{D} = M_w/M_n$

e: Duration 16 h

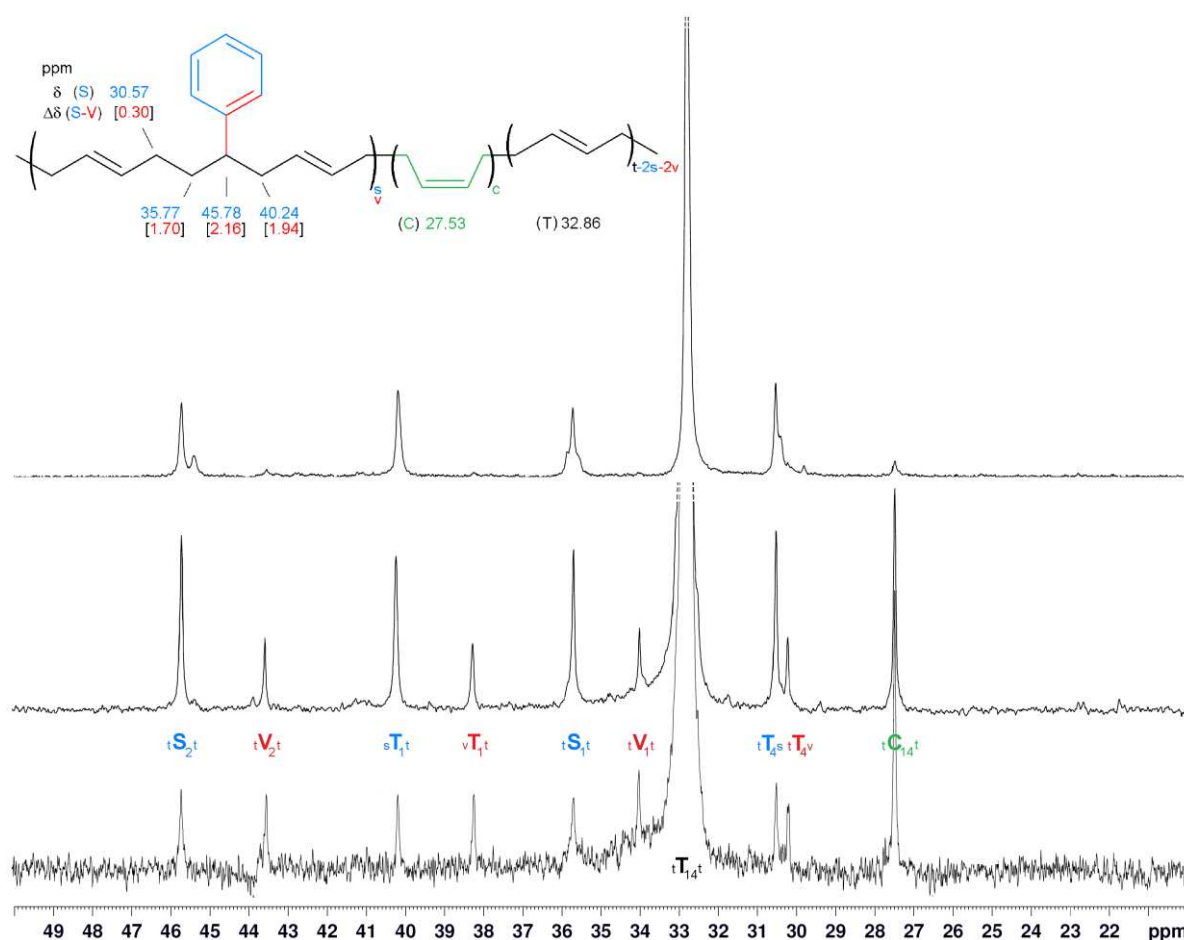
From the presence of new peaks on the NMR spectra (figure 5) attributed to the junction motives, we assume that the isolated material was a copolymer containing butadiene and styrene units linked to each other, and not a blend of the two homopolymers (table 3). As expected from our experience in styrene/isoprene copolymerization, the insertion rate of the styrene co-monomer was lower than the diene one. Indeed, even with a high initial styrene concentration ([B]/[S] = 20/80), the insertion percentage of styrene in the copolymer (calculated from the <sup>1</sup>H spectrum of the copolymer, figure 4) remained quite low (16.9%, run 17). With similar catalytic combinations made of the same pre-catalysts, we found that up to 32% of styrene could be inserted in polyisoprene with a I/S feed ratio of 20/80 (I for isoprene) [45].



**Figure 4.**  $^1\text{H}$  NMR spectrum of a poly(butadiene-*co*-styrene) containing 16.9 % of styrene in the copolymer (run 17,  $\text{C}_2\text{D}_2\text{Cl}_4$ , \* solvent impurities and residual H resonance).

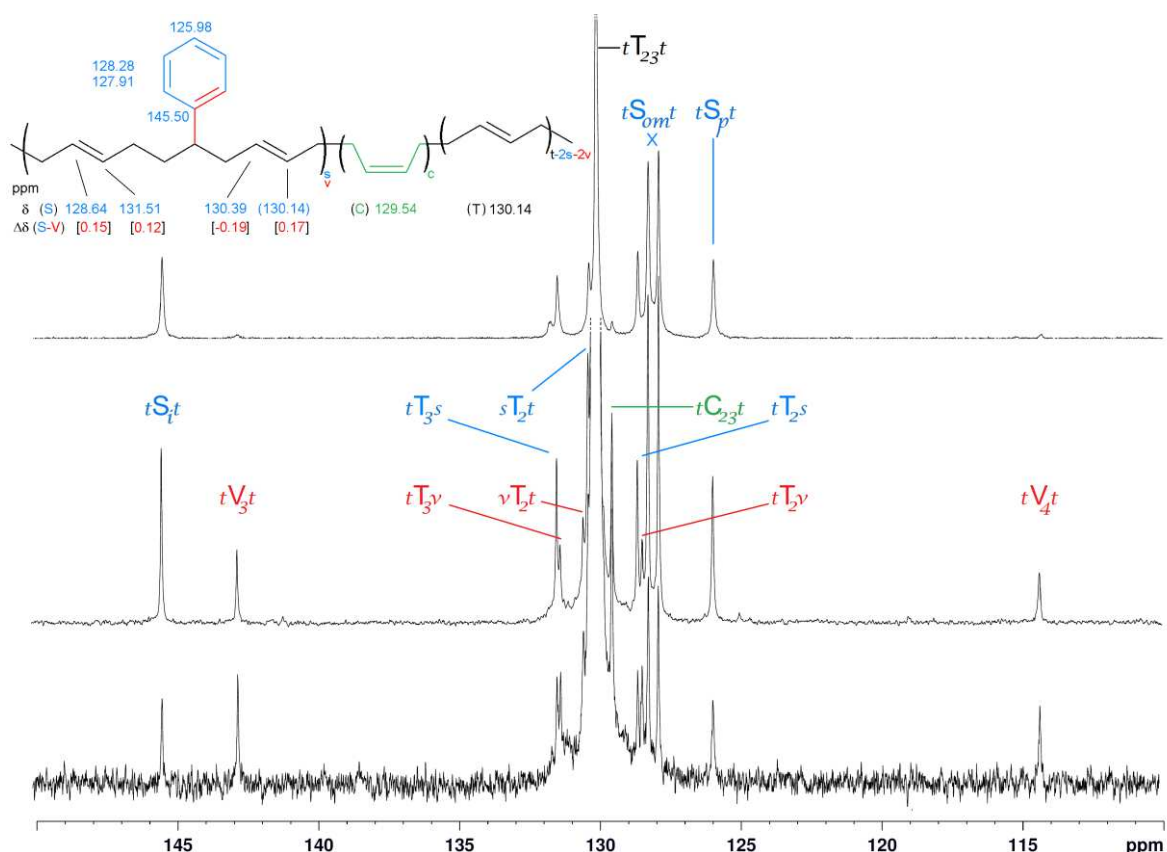
The microstructure of the polybutadiene backbone of the copolymers was determined from  $^{13}\text{C}$  NMR. On figures 5 and 6 are represented the spectra for copolymers containing 1.4, 3.8, and 16.9 % of styrene units (runs 18, 16, and 17, respectively). The spectra of the copolymer samples all display the typical signals of *trans*-polybutadiene along with inserted styrene units. Assignments were done by reference to the above described homopolybutadiene (*trans* selective with low amounts of vinyl and *cis* defects, see Figures 1 and 2) and to poly[(*trans*-butadiene)-*co*-styrene] with low amounts of styrene [14]. From a NMR point of view, an analogy can be seen between a styrene unit inserted in *1,4-trans* regular chains compared with a vinyl defect in the same type of chains. In particular, the signals of the main chain were found simply shifted by a few ppm when changing the branching from vinyl to phenyl. The shift of resonances from vinyl to phenyl branches were about 2 ppm for the branched carbon and its neighbors, of 0.3 ppm for the next  $\text{sp}^3$  carbon and of about 0.15 ppm for each  $\text{sp}^2$  carbons, all in the down field direction except for the nearest  $\text{sp}^2$  carbon. It is noteworthy that very few examples of such copolymers of styrene with butadiene in a *trans*- configuration were reported in the literature [14]. By view of the narrowness of the peaks, and particularly the signal of the *ipso* carbon ( $\delta = 145.50$  ppm), a micro-structure made of single styrene units

into *trans*-PB sequences can be advanced, similarly as observed in the case of isoprene/styrene copolymerization with catalysts of the same family [45]. Such insertions of isolated styrene in *trans*-PB sequences (TTTSTTT) contrast with some reports of styrene inserted in *cis*-PB by the fact that the styrene insertions were followed by a singular *trans* unit (CCCSTCCC) [44,65].



**Figure 5.**  $^{13}\text{C}$  NMR spectrum of poly(butadiene-*co*-styrene) samples isolated from runs 18, 16, and 17 (from bottom to top), containing 1.4, 3.8, and 16.9 % of styrene, respectively (C  $\text{sp}^3$  region,  $\text{CDCl}_3$ ).



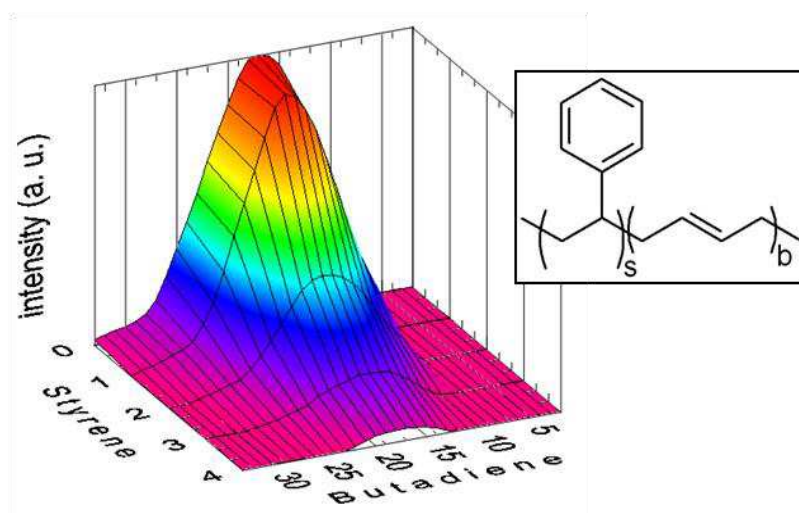


**Figure 6.**  $^{13}\text{C}$  NMR spectrum of poly(butadiene-*co*-styrene) samples isolated from runs 18, 16, and 17 (from bottom to top), containing 1.4, 3.8, and 16.9 % of styrene, respectively (C  $\text{sp}^2$  region,  $\text{CDCl}_3$ ).

The highest rate of *1,4-trans* stereoregularity is obtained for Mg/Nd ratio of 1 (runs 16-18). Like for isoprene-styrene copolymerization with the same catalytic system [45], the initial percentage of styrene monomer in the feed has no significant influence on the selectivity, which is maintained at more than 95 % *1,4-trans*. In conditions of polymer chain transfer, *i.e.* with an excess of BEM (runs 19, 20), the higher the  $[\text{Mg}]/[\text{Nd}]$  ratio, the lower the copolymerization yield. This result is similar to the one obtained in the case of butadiene homopolymerization (tables 1 and 2). Regarding the macromolecular data, polymer chain transfer is established by the comparison of the  $M_n$  values, decreasing of one order of magnitude (runs 19, 20) in the presence of excess of BEM. However, this doesn't strictly match with the number of alkyl initiating groups, and therefore one can conclude that the transfer doesn't take place in controlled and reversible CCG (Catalyzed Chain Growth) conditions, as also shown by the quite broad polydispersities measured [54]. Regarding the copolymer microstructure, the  $[\text{Mg}]/[\text{Nd}]$  ratio has several effects that can be considered at two levels: the polybutadiene backbone on the one side, and the styrene insertion rate and distribution on the other side. With equal quantity of both monomers in the feed, increasing the  $[\text{Mg}]/[\text{Nd}]$  ratio decreases the *1,4-trans*-stereoregularity of the polybutadiene backbone, to

the advantage of the rate of 1,2- regio errors. This trend was similar for the homopolymerization (table 1 and 2), and the effect seems to be less pronounced in copolymerization (run 14 vs run 20, 83.1% vs 87.3% 1,4-*trans*). Finally, the styrene insertion rate is increased at high Mg/Nd ratios for equal monomers quantity in the feed (runs 16, 19, 20). These results confirm the concept of a control of the relative comonomer reactivity / microstructure by CCTP (coordinative chain transfer copolymerization) [66,67,46].

In order to compare the facility of insertion of each monomer at the beginning of the reaction, a low  $M_n$  copolymer was synthesized with feed ratio  $[B]/[S] = 20/20$  and a short reaction time (15 min), and submitted to MALDI-TOF analysis. For the sake of better detection, this copolymer was functionalized with an anthrone end-group (see experimental section and Supplementary Data for details). Since the precise molar mass of each chain, together with their isotopic distribution, were able to be discerned from the mass spectrum, their exact composition was deduced, in particular the exact number of each monomer units in the oligomeric chains (fig. 7). New clues were hence obtained of the controlled character of the polymerization: first, each chain included the desired initiator (and not another, which would arise from an uncontrolled transfer process); second, functionalization occurred (albeit at an unknown rate, since dead chains were not detected); and, last but not least, statistical distributions of styrene and butadiene monomers were observed, that follow exactly the Poisson probability. The lower styrene insertion rate, as compared to the butadiene one, was confirmed: the average degree of polymerization, after a 15-minute reaction, was between 17 and 18 for butadiene monomer whereas it was between 1 and 2 for styrene monomer.



**Figure 7.** MALDI-TOF cumulative diagram of a poly(butadiene-*co*-styrene) oligomer.

## Conclusion

Butadiene homopolymerization was performed with a catalytic system based on borohydrido neodymium complexes associated with butylethylmagnesium. The polybutadiene obtained is highly *trans*-stereoregular, up to 96.7% according to thorough NMR analyses. In the presence of an excess of alkylating agent, chain transfer reactions between neodymium and magnesium are evidenced, along with appearance of 1,2 regio-defects. Butadiene-styrene copolymerization was achieved with the same catalytic system, showing the formation of poly(butadiene-*co*-styrene) copolymers with up to ca 17% of inserted styrene. Whatever the amount of styrene in the feed, the polybutadiene backbone remained *trans*-regular, and no occurrence of styrene-styrene junctions were found. Excess of BEM causes a decrease of activity, and a slightly higher styrene insertion rate, extending the range of application of the comonomer reactivity control by the CCTP concept.

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